Short communication

Fe–air rechargeable battery using oxide ion conducting electrolyte of Y_2O_3 stabilized ZrO_2

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HIGHLIGHTS

► SOFC concept was applied for Fe–air rechargeable battery by using H_2/H_2O as a mediator.
► 10 cycles of charge–discharge were performed over the 250 mAh g^{-1}-Fe.
► Observed P_{O_2} suggested that FeO was formed in discharge and reduced to Fe.
► Impedance analysis suggested that cell was highly stable during charge–discharge.

ARTICLE INFO

ABSTRACT

Solid oxide fuel cell concept was applied for Fe–air rechargeable battery by using H_2/H_2O as a mediator for Fe redox. Oxygen partial pressure in Fe set chamber during discharge was monitored simultaneously with O_2 sensor for analysis of discharge mechanism. On the cell consisting of Pt anode, Y_2O_3 stabilized ZrO_2(YSZ) electrolyte, and Pt cathode, 10 cycles of charge and discharge was stably performed, although decrease in capacity was observed at initial cycle. Oxygen partial pressure (P_{O_2}) was monitored by zirconia oxygen sensor which is used for Fe set chamber. Simultaneous monitoring the oxygen partial pressure during the charge and discharge, the reasonable response of P_{O_2} in Fe set chamber was observed and for discharge, Fe seems to be oxidized to FeO and reduction to Fe was also confirmed. Impedance plots suggested that degradation could be assigned to the increased diffusion overpotential because of the decreased oxidation rate of Fe powder. However, after second cycles, internal resistance of the cell was stable up to 10 cycles examined. Therefore, application of SOFC concept and H_2/H_2O redox mediator is successfully demonstrated for the Fe–air rechargeable battery.

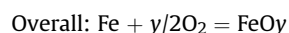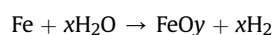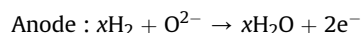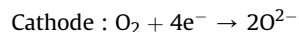© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Recently, rechargeable battery with large capacity are strongly requested from the energy storage and averaging the electric power from renewable energy like solar cell or wind mill power generator etc. At present, Li-ion or NaS battery is considered for this purpose. Metal–air battery is attracting attention as the alternative battery with large capacity because cathode active material, oxygen, is no necessary stored in the battery. At present, there are many attention for Li–air battery [1–6]. However, because of insufficient

reversibility of electrode reaction, cycle stability is still serious issues to overcomes for Li–air battery [6]. In contrast, Fe–air battery have also been studied by using aqueous alkaline electrolyte [7,8]. Comparing with Li–air battery, theoretical energy density of Fe–air battery is much smaller (932 Wh kg^{-1}-Fe at 1273 K assuming FeO formation), but it is much larger than that of Li-ion battery. In addition, Fe is large natural abundance, cheap and harmless and so low impact for environment. Therefore, Fe–air battery is also interesting battery from environmental compatibility, safety, and large energy density [8]. In the conventional study, alkaline aqueous electrolyte (OH ion conductor) is generally used. However, because of H_2 formation during charge and the conductivity of electrolyte is decreased by CO_2 in air, Fe–air battery is considered to be primary battery [9,10]. Since Fe oxidation potential is almost the same with that of H_2 and so, when oxide ion conductor could be used for electrolyte, the issues for Fe–air

rechargeable battery could be solved because solid electrolyte for SOFC is highly stable. However, large volumetric change occurs during redox of Fe [11,12] and so simple application of oxide ion conductor can not be achieved Fe–air rechargeable battery. Therefore, the electrode and active material should be separated. The combination of solid oxide fuel cells technology with redox of Fe through H_2/H_2O mediator is promising way to this purpose. Recently, Xu et al. reported that the combination of SOFC technology with Fe–air rechargeable battery by using tubular cell with YSZ electrolyte [13]. We also reported the similar concept by using $LaGaO_3$ based electrolyte [14]. On this concept for Fe–air battery, it is expected that charge and discharge is performed by the following equations;

Cathode : $O_2 + 4e^- \rightarrow 2O^{2-}$

Anode : $xH_2 + O^{2-} \rightarrow xH_2O + 2e^-$

$Fe + xH_2O \rightarrow FeOy + xH_2$

Overall: $Fe + y/2O_2 = FeOy$

From viewpoint of overall reaction, Fe and oxygen are active material for battery and so, battery could be classified as metal–air battery. Here, it is clear that H_2/steam works as a mediator, not battery active material because discharge capacity monotonically increased with increasing Fe amount and almost negligible capacity observed without Fe [14]. Therefore, from battery classification, this battery could be classified as one kind of redox flow battery or more suitable as Fe–air battery.

However, details of discharge and charge mechanism and also oxidation state of Fe are not studied in details. It is well known that oxidation state of Fe strongly depends on the temperature and oxygen partial pressure (P_{O_2}) from the Keringum diagram. Therefore, monitoring P_{O_2} during charge–discharge is important for estimating the reaction occurred during discharge and charge. On the other hand, changes in internal resistance of the cell during charge–discharge have not been studied in details. Therefore, we applied ac impedance method for the analysis of internal resistance during charge and discharge. One of the issues to overcome in this battery is obviously the low cycle stability in anodic electrode because Ni based anode is reoxidized and suffered from the serious damage because of aggregation and delamination. Since Pt is not easily reoxidized by high P_{O_2}, we used Pt/YSZ/Pt for Fe–air rechargeable battery and studied cycle stability, and also measured P_{O_2} simultaneously with charge–discharge, in order to confirm the cell works as we designed.

2. Experiments

Fig. 1 shows the schematic view of the experimental set up used in this study. Electrolyte support planar type single cell (17 mm in diameter and 0.3 mm thickness) was used in this study and 8 mol% Y_2O_3 stabilized ZrO_2 (YSZ, Tosoh) was used for electrolyte. The powder of YSZ was pressed into disk followed by sintering at 1673 K for 6 h. YSZ disk was polished to 0.3 mm in thickness. Pt was used for anode and cathode. Pt paste (TR-7902, TANAKA KIKINZOKU KOGYO) was painted on each face of YSZ disk with 5 mm diameter followed by calcination at 1273 K for 30 min. The prepared planer type single cell was set between Al_2O_3 tube with molten Pyrex glass as a gas sealant. In the bottom of the cell, Ca stabilized ZrO_2 (CSZ) tube (8 ml in volume) was set with molten glass gas seal for monitoring P_{O_2}. Fe oxide (Fe_3O_4, 50 mg, Wako Co. Ltd, chemical reagent class) was set in CSZ tube as an oxygen sensor. After heating the cell to 1273 K, humidified nitrogen (Saturated H_2O at 353 K in
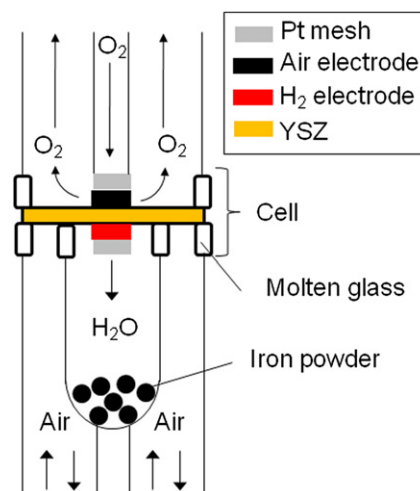

Fig. 1. Schematic view of experimental set up fabricated.

50 ml min^{-1} of N_2) was fed into the Fe set chamber. Therefore, at 1273 K, Fe set chamber is also sealed with molten grass and filled with steam for the mediator of Fe redox. Charge and discharge was measured with 4 probed method under applying the constant voltage, 1.5 V for charge, and constant current, 50 mAcm^{-2} for discharge. For testing, the electrochemical contacts were achieved with Pt wire and Pt mesh. Impedance spectra were measured in open circuit condition with a frequency range of 0.1 HZ–0.1 MHz and 10 mV ac amplitude with Sorlartron 1260/1287 impedance analyzer.

3. Results and discussion

Fig. 2 shows first charge curve and oxygen partial pressure in the iron set room. After applying potential to charge, P_{O_2} in Fe set chamber was drastically decreased and achieved P_{O_2} was lower than $10^{-17.5}$ atm, which was reasonable value of H_2–H_2O. Therefore, generation of H_2 by steam electrolysis was successfully occurred. Because metallic state of Fe is stable at this P_{O_2}, and 1273 K, Fe was successfully reduced by H_2/H_2O mediator.

Fig. 3 shows first discharge curve and P_{O_2} in Fe set chamber. After applying current to discharge, 0.56 V of potential plateau was observed. In this potential plateau, P_{O_2} was also stable. Therefore, this is typical shape of chemical equilibrium between Fe and O_2. Observed P_{O_2} in potential flat was estimated to be around
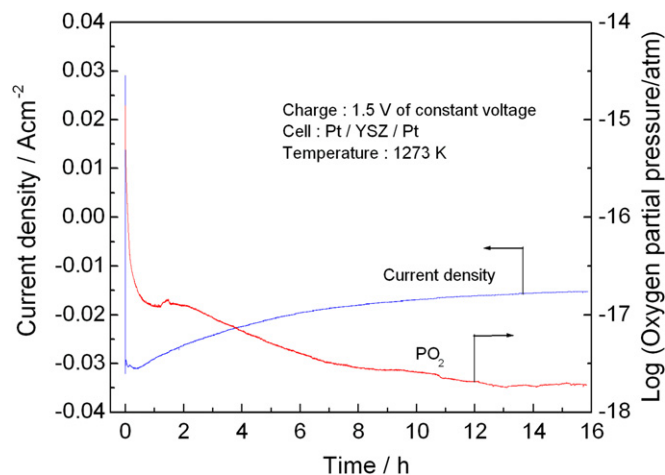

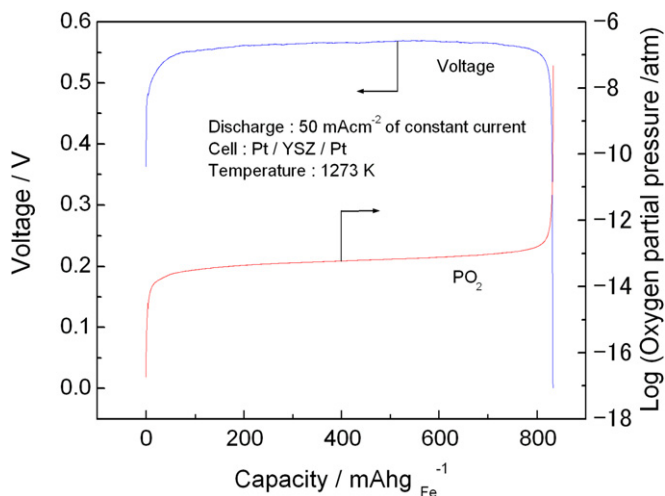**Fig. 2.** First charge curve and oxygen partial pressure in Fe set room.

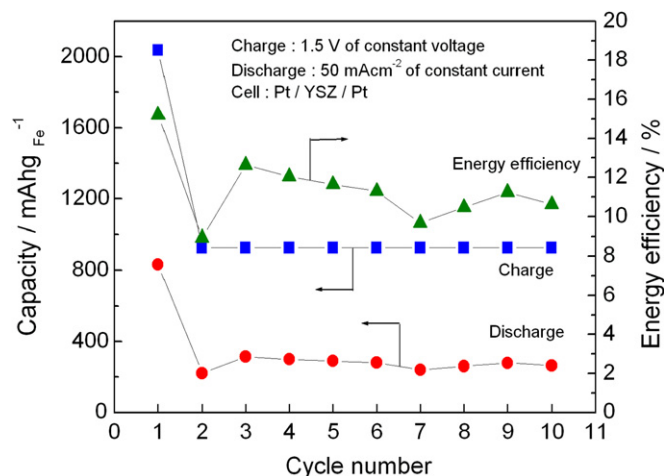**Fig. 3.** First discharge curve and oxygen partial pressure in Fe set room.

Fig. 5. Cycle stability of the Fe–air cell using YSZ electrolyte.

10^{-13} atm, and so the stable species of Fe oxide at this P_{O_2} is assigned to FeO, which corresponded to 960 mAh g^{-1} of the theoretical capacity as shown in Fig. 4. Therefore, at the present cell, the observed capacity at the first cycle (830 mAh g^{-1}-Fe) is 86% of the theoretical capacity of FeO. It is also confirmed that the discharge capacity by oxidation of H_2 is negligibly small and so H_2 in Fe set chamber works as redox mediator.

Fig. 5 shows a cycle stability of Fe–air cell using YSZ electrolyte. Although the decrease in capacity was observed at second cycle, 250 mAh g^{-1}-Fe of capacity was sustained for 10 cycles with electrochemical charge and discharge. Observed P_{O_2} of Fe set chamber in the end of charge and discharge were always lower than 10^{-17} atm and higher than 10^{-5} atm, respectively.

Considering estimated P_{O_2} during discharge, FeO seems to be dominant oxide phase of Fe and so the observed capacity of the cell after 2nd cycles is 23% of the theoretical value of FeO formation. The reason why Fe oxidation amount is decreased after 2nd cycle is not clear, however, it assumed that sintering of Fe powder may relate, i.e., reaction rate of Fe powder with steam was decreased by

decreasing surface area of Fe powder. In any way, redox of Fe by charge–discharge was almost reversible and so the concept of rechargeable Fe–air battery using oxide ion conductor was successfully demonstrated. However, energy efficiency for charge and discharge was low, around 10%. There are some reasons for low efficiency. One is that there is large internal resistance (IR) of the cell because of thick YSZ electrolyte and low activity of electrode. Second one is reversibility of redox of Fe is low because of decreasing surface area due to the sintering of Fe and third is low activity of Pt electrode used [15].

Fig. 6 shows impedance plots of the cell before and after the first charge. At initial, large semicircle at lower frequency lower than 1 Hz was observed. It seems to be assigned to the diffusion overpotential of H_2. After the first charge, observed overpotential lower than 1 Hz was drastically decreased and so H_2 was successfully formed by electrolysis and reduction of Fe seems to be occurred. The main resistance is dominated by electrode resistance because Pt is not so active. It is also noted that IR loss of electrolyte at the high frequency intercept is 0.3 Ω cm^{-2}, which is reasonable value of IR loss calculated from the conductivity of YSZ at 1273 K.

Fig. 7 shows impedance plots of the cell after charge. Although there was a little increase in overpotential, reversibility in
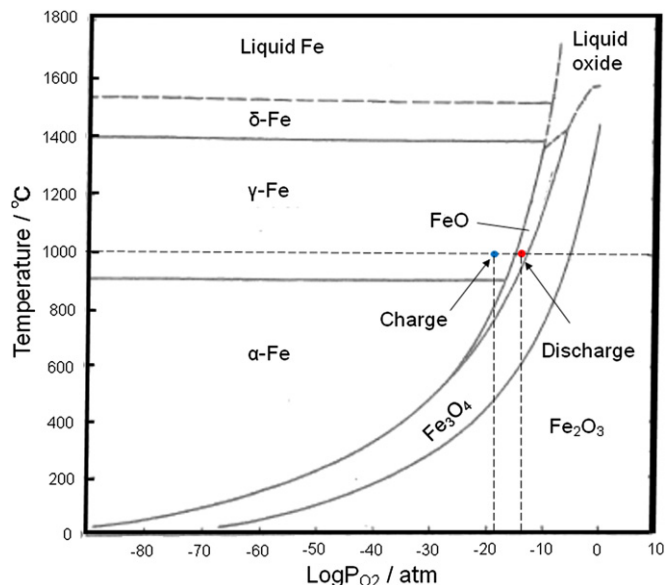

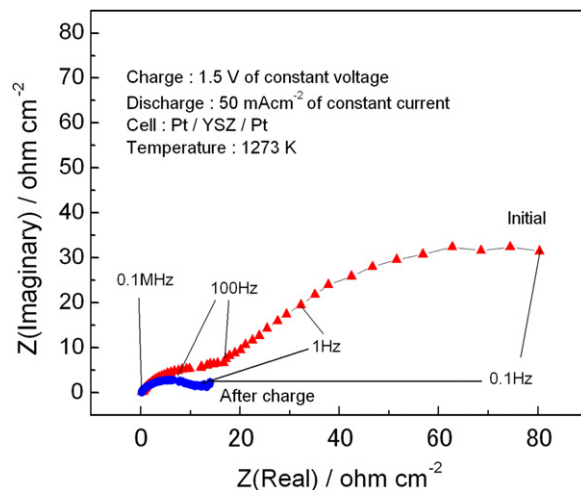**Fig. 4.** Keringum diagram of Fe–O_2 and P_{O_2} in charge and discharge.

Fig. 6. Impedance spectra of the cell before and after the 1st discharge at open circuit voltage.
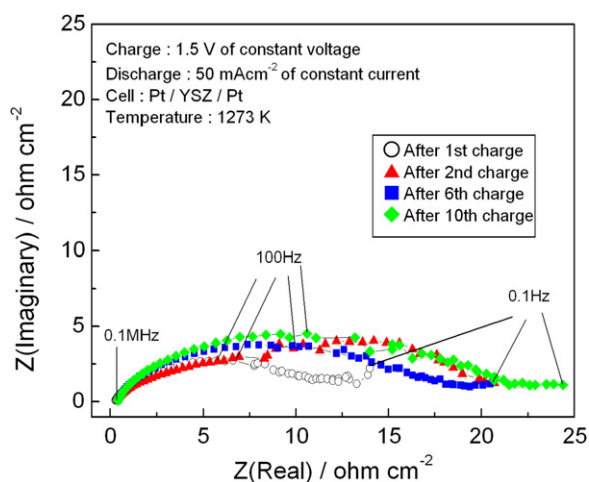
Fig. 7. Impedance spectra of the cell after the discharge at open circuit voltage.
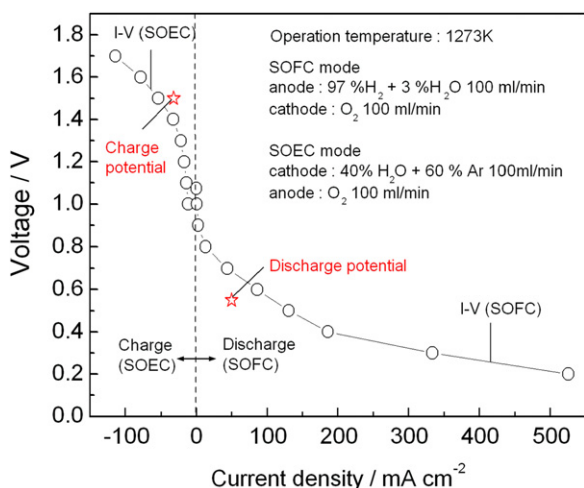

Fig. 8. Comparison of *I–V* property between the Fe—air cell (present study) and the same cell under SOFC and SOEC with gas flow system.

impedance plot was observed. A small increase in electrode resistance after several cycle may be assigned to the diffusion overpotential, which was caused by the insufficient amount of H_2 by the decreased oxidation of Fe by sintering. It is also noted that IR loss at the high frequency intercept are almost the same in the following cycles. Therefore, YSZ electrolyte is highly stable even in long term operation with high potential (1.5 V).

Fig. 8 shows charge and discharge potential of Fe—air cell compared with SOEC—SOFC mode (H_2O/H_2 gas flow system). Fe—air cell also showed high reversibility for charge mode, and discharge mode. Charge and discharge potential were 1.5 V (at minus 31 mAcm^{-2}) and 0.55 V (at 50 mAcm^{-2}), respectively. The difference between potential for the gas flow system of SOFC, SOEC and that in Fe—air cell is assigned to the diffusion overpotential of H_2 because of lower concentration of H_2 from Fe powder. Therefore, cell structure is need to be more considered for decreasing gas diffusion

overpotential. Such as distance between Fe powder and oxide ion conductor, and volume of the Fe set room obviously affects the cell performance and requested to make smaller. This is now under studied. In any way, it is evident that Fe—air rechargeable battery was successfully demonstrated by combination of SOFC technology with Fe oxidation.

4. Conclusions

Rechargeable Fe—air battery using Pt/YSZ/Pt for electrolyte was investigated. 10 cycles of charge—discharge were performed over the 250 mAh g^{-1}-Fe of capacity. Monitored P_{O_2} in Fe set room were $10^{-17.5}$ and 10^{-13} atm after the charge and discharge, respectively. Therefore, the H_2/H_2O mediator was successfully worked for Fe—air cell and formed Fe oxide seems to be FeO from P_{O_2} during discharge and Keringum diagram. Impedance plots of the cell also suggested that H_2 formation during charge as a decrease in diffusion overpotential at low frequency region. Degradation of the cell was not so significant and almost the same resistance were observed after several cycles. Difference in potential between SOFC—SOEC mode and Fe—air cell assigned to the diffusion overpotential caused by the low activity of Pt electrode and also slow oxidation rate of Fe powder. Therefore, improved electrode activity and improved oxidation rate for Fe powder could be effective for increasing potential of Fe—air battery using oxide ion conductor, YSZ for electrolyte.

References

[1] K.M. Agraham, Z. Jiang, Journal of Electrochemical Society 143 (1996) 1.
[2] A. Kraytsberg, Y. Ein-Eli, Journal of Power Sources 196 (2011) 886—893;
    R.A. DeSouza, J.A. Kilner, Solid State Ionics 106 (1998) 175.
[3] B. Dunn, H. Kamath, J.M. Tarascon, Science 18 (2011) 928.
[4] S.A. Freunberger, Y. Chen, Z. Peng, J.M. Griffin, L.J. Hardwick, F. Barde, P. Novak, P.G. Bruce, Journal American Chemical Society 133 (2011) 8040.
[5] Y.-C. Lu, H.A. Gasteiger, Y. Shao-Horn, Journal American Chemical Society 133 (2011) 19048.
[6] A.K. Thapa, T. Ishihara, Journal of Power Sources 196 (2010) 7016.
[7] B.T. Hang, S.H. Yoon, S. Okada, J. Yamaki, Journal of Power Sources 168 (2007) 522.
[8] A. Ito, L. Zhao, S. Okada, J. Yamaki, Journal of Power Sources 196 (2011) 8154.
[9] S.J. Skinner, J.A. Kilner, Solid State Ionics 135 (2000) 709.
[10] N. Jayalakshmi, V.S. Muralidharan, Journal of Power Sources 32 (1990) 277 (W. Hui, S. Takenaka).
[11] T. Hatae, M. Matsushita, S. Yamashita, Soid State Ionics 180 (2009) 1305.
[12] M. Ettler, H. Timmermannb, J. Malzbendera, A. Weber, N.H. Menzler, Journal of Power Sources 195 (2010) 5452.
[13] N. Xu, X. Li, X. Zhao, J.B. Goodenough, K. Huang, Energy and Environmental Science 4 (2011) 4942.
[14] A. Inoishi, S. Ida, T. Ishihara, 220th Electrochemical Society Meeting 466, 2011.
     A. Inoishi, S. Ida, S. Uratani, T. Okano, Tatsumi Ishihara, Physical Chemistry Chemical Physics 14 (2012) 12818.
[15] W. Hui, S. Takenaka, K. Otsuka, International Journal of Hydrogen Energy 31 (2006) 1733.